Environmentally Assisted Cracking of Commercial Ni-Cr-Mo Alloys - A Review

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ENVIRONMENTALLY ASSISTED CRACKING OF COMMERCIAL Ni-Cr-Mo ALLOYS
A REVIEW

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ABSTRACT

Nickel-Chromium-Molybdenum alloys (Ni-Cr-Mo) are highly resistant to general corrosion, localized corrosion and environmentally assisted cracking (EAC). Cr acts as a beneficial element under oxidizing acidic conditions and Mo under reducing conditions. All three elements (Ni, Cr and Mo) act synergistically to provide resistance to EAC in environments such as hot concentrated chloride solutions. Ni-Cr-Mo alloys may suffer EAC in environments such as hot caustic solutions, hot wet hydrofluoric acid (HF) solutions and in super critical water oxidation (SCWO) applications. Not all the Ni-Cr-Mo alloys have the same susceptibility to cracking in the mentioned environments. Most of the available data regarding EAC is for the oldest Ni-Cr-Mo alloys such as N10276 and N06625.

Keywords: Environmentally Assisted Cracking, Nickel-Chromium-Molybdenum Alloys, Alkalis, Wet Hydrofluoric Acid, Supercritical Water Oxidation.

INTRODUCTION

Environmentally Assisted Cracking (EAC) is a general term that includes events such as stress corrosion cracking (SCC), hydrogen embrittlement (HE), sulfide stress cracking (SSC), liquid metal embrittlement (LME), corrosion fatigue (CF), etc. EAC refers to a phenomenon by which a normally ductile metal looses its toughness (e.g. elongation to rupture) when it is subjected to mechanical stresses in presence of a specific corroding environment. For EAC to occur, three affecting factors must be present simultaneously. These are: (1) Mechanical tensile stresses, (2) A susceptible metal microstructure and (3) A specific aggressive environment. If any of these three factors is removed, EAC will not occur. That is, to mitigate the occurrence of EAC, engineers may, for example, eliminate residual stresses in a component or, limit its application to certain non-aggressive chemicals (environment). The term environment not only includes the chemical composition of the solution in contact with the component but also other variables such as temperature and the redox potential in the system.

Nickel alloys are in general more resistant than stainless steels to EAC. Austenitic stainless steels (such as S30400) suffer SCC in presence of hot aqueous solutions containing chloride ions. Since chloride

ions are ubiquitous in most industrial applications, the use of stainless steels components containing sometimes only minimal residual stresses is seriously limited because of the chloride cracking. On the other hand, nickel alloys (such as C-276) are to all intents and purposes immune to SCC in presence of hot chloride solutions and therefore an excellent alternative to replace the troubled austenitic stainless steels. Nickel alloys may be prone to EAC in other environments such as hot caustic and hot wet hydrofluoric acid. [1-2] Nevertheless, the conditions where nickel alloys suffer EAC are more specific than for austenitic stainless steels and therefore avoidable by the proper design of the industrial components.

THE FAMILY OF NICKEL ALLOYS

Nickel-based alloys are solid solutions based in the element nickel (Ni). Even though Ni-based alloys in general contain a large proportion (sometimes up to 50%) of other alloying elements, nickel alloys still maintain the face centered cubic lattice structure (FCC or gamma) from the nickel base element. As a consequence of the FCC structure, nickel based alloys have excellent ductility, malleability and formability. Nickel alloys are also readily weldable. There are two large groups of the commercial Ni-based alloys. One group was designed to withstand high temperature and dry or gaseous corrosion while the other is mainly dedicated to low temperature (aqueous) applications. Nickel based alloys used for low temperature aqueous or condensed systems are generally known as corrosion resistant alloys (CRA) and nickel alloys used for high temperature applications are known as heat resistant alloys (HRA) or high temperature alloys (HTA). The practical industrial boundary between high and low temperature nickel alloys is in the order of 500°C (or approximately 1000°F). Most of the nickel alloys have a clear use either as CRA or HRA; however, a few alloys can be used for both applications (e.g. alloy 625 or N06625).

HEAT RESISTANT ALLOYS

Unlike CRA, which are mostly selected for their capacity to resist corrosion in a given environment, most HRA need to play a dual role. Namely, besides their capacity to withstand the corrosive aggressiveness of the environment, HRA also need to keep significant strength at high temperatures. In many instances, for example near and above 1000°C, alloy selection is dominated by how strong the alloy is in this temperature range. There are many different industrial high temperature environments. In general, practical use has divided these environments according to the most common causes of failure of a component in service. [3-4] The most common failures are associated to the attack by a specific element such as oxygen (which causes oxidation), carbon (carburization and metal dusting), sulfur (sulfidation), halogen (e.g. chlorination) and nitrogen (nitridation). Other modes of failure such as molten metal attack and hot corrosion, are less specific. The most common high temperature degradation mode is oxidation and the protection against oxidation in general is given by the formation of a chromium oxide scale. In many instances, the presence of a small amount of aluminum or silicon in the alloy may improve the resistance against oxidation of a chromia-forming alloy. Attack by other elements such as chlorine, sulfur, etc. will depend strongly on the partial pressure of oxygen in the environment. [4] Due to their application, failures of HTA in service are not usually associated with environmentally assisted cracking since they may not be in contact with a condensed phase promoting cracking. A few HTA are used in the handling of liquid metals (such as in liquid Zn galvanizing) and therefore may suffer embrittlement by liquid metal. The most common Ni-Cr-Mo alloy that may be associated to high temperature applications is Alloy 625.

CHEMICAL COMPOSITION AND CORROSION BEHAVIOR OF
CORROSION-RESISTANT NICKEL ALLOYS

Nickel alloys are highly resistant to corrosion, and in most environments nickel alloys outperform the most advanced stainless steels. One of the reasons is because nickel can be alloyed more heavily than iron. That is, large amounts of specific elements can be dissolved purposely into nickel to tailor the alloy for a particular environment. In general, industrial environments can be divided into two broad categories, reducing and oxidizing. These terms refer to the range of electrode potential that the alloys experience, which is controlled by the cathodic reaction in the system. Thus, a reducing condition is generally controlled by the discharge of hydrogen from a reducing acid such as hydrochloric acid. An oxidizing environment has a potential that is higher than the potential for hydrogen discharge. This potential may be established by cathodic reactions such as reduction of dissolved oxygen (O_2) from the atmosphere, chlorine gas (Cl_2), hydrogen peroxide (H_2O_2), chromates or chromic acid (CrO_4^{2-}), nitrates or nitric acid (NO_3^-) and metallic ions in solution such as ferric (Fe^{3+}) and cupric (Cu^{2+}). Nickel alloys, the same as other alloys, may suffer two main types of corrosion, uniform corrosion and localized corrosion. Uniform corrosion may happen under reducing conditions in the active region of potentials and also under oxidizing conditions in the form of a slow passive dissolution. Localized corrosion such as pitting and crevice corrosion generally occurs under oxidizing conditions. Stress corrosion cracking (SCC) or environmentally induced cracking could occur at any electrochemical potential range. In many alloy systems, SCC is also associated to specific potential windows, for example, in the anodic region above a critical potential of in the cathodic region, also below a threshold potential.

From the chemical composition point of view, corrosion resistant Ni-based alloys can be grouped as: (1) commercially pure nickel, (2) Ni-Cu alloys, (3) Ni-Mo alloys, (4) Ni-Cr-Fe alloys and (5) Ni-Cr-Mo alloys. A brief description of the corrosion behavior and application of each group of alloys is given below. Details can be found elsewhere. [5-6] The main widely accepted application of commercially pure nickel is the handling of highly concentrated and hot caustic solutions (alkalis). Nickel has lower corrosion rates in hot caustic solutions than alloyed nickel since alloying elements such as Cr and Mo dissolve preferentially from the Ni-alloys in hot caustic solutions. Nickel can also tolerate well cold reducing acids because of the slow discharge of hydrogen on its surface. Hot reducing acids and oxidizing acids corrode pure nickel rapidly. The main application of Ni-Cu alloys (or Monel© alloys) is in the handling of pure hydrofluoric acid. However, if oxidants such as oxygen are present in hydrofluoric acid, Ni-Cu alloys may suffer intergranular attack. [7] Ni-Cu alloys are slightly more resistant to general corrosion than Ni-200 in hot reducing and oxidizing acids such as sulfuric acid and nitric acid. Ni-Mo alloys, commonly known as Hastelloy B type alloys, were specifically developed to withstand reducing HCl at all concentrations and temperatures. Besides more expensive materials such as tantalum, Ni-Mo alloys are the best alloys for hot hydrochloric acid. [5,8-9] Ni-Mo alloys are also used in the handling of other corrosive reducing environments such as sulfuric, acetic, formic, hydrofluoric and phosphoric acids. However, Ni-Mo alloys perform poorly in oxidizing acids or, for example, in hydrochloric acid contaminated with ferric ions. [8] The Ni-Cr-Fe family is large and includes alloys such as Inconel 600 (N06600) and 690 (N06690) which are purely Ni-Cr-Fe alloys. However, this family also includes alloys that may contain smaller amounts or molybdenum and/or copper (such as alloy G-30-N06630 ©and 825-N08825). Ni-Cr-Fe alloys in general are less resistant to corrosion than Ni-Cr-Mo alloys; however, they could be less expensive and therefore find a wide range of industrial applications. The corrosion rate of alloy 600

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in sulfuric acid is higher than the corrosion rate of Alloy 825, for example. The latter contains small amounts of molybdenum and copper, which are beneficial alloying elements for resistance to sulfuric acid. Also, Alloy 825 has lower corrosion rate than Alloy 600 in nitric acid since it contains larger amount of chromium. One of the most common applications of Ni-Cr-Fe alloys such as Alloy G-35 (N06035), [10] Alloy 33 (R02033), [11] Alloy 31 (N08031) [12] and Hastelloy G-30 is in the industrial production of phosphoric acid and in highly oxidizing media such as nitric acid.

The General Corrosion Behavior of Ni-Cr-Mo Alloys

There are many commercially available Ni-Cr-Mo alloys today. All these alloys were derived from the original C alloy (N10002), which was introduced to the market in cast form in 1932. The more advanced Ni-Cr-Mo alloys are Inconel 686, Nicrofer 5923 and Hastelloy C-2000. [9] Some of the most recent additions to the family of Ni-Cr-Mo alloys include Alloy MA21 (N06210) and a high mechanical properties version of N06022. [13] However, the more common Ni-Cr-Mo alloy in industrial applications is Alloy C-276, which was introduced in the market in the mid 1960s. Ni-Cr-Mo alloys are the most versatile corrosion resistant nickel alloys since they contain molybdenum for protection against corrosion under reducing conditions and chromium, which protects against corrosion under acidic oxidizing conditions. [8-9] For example, C-276 has low corrosion rates both in reducing conditions (boiling 10% sulfuric acid) and oxidizing conditions (boiling 10% nitric acid). One of the major applications of Ni-Cr-Mo alloys is in presence of hot chloride containing solutions. Under these conditions, most of the stainless steels would suffer crevice corrosion, pitting corrosion and stress corrosion cracking. However, Ni-Cr-Mo alloys such as alloys C-22, 59, 686, etc. are highly resistant if not immune to chloride induced attack in most industrial applications. [5]

ENVIRONMENTS THAT MAY CAUSE CRACKING IN Ni-Cr-Mo ALLOYS

Table 1 shows that Ni-Cr-Mo alloys possess great toughness, that is, their UTS values are near 1000 MPa and their elongation to rupture are generally higher than 50%. That is, in an inert environment, Ni-Cr-Mo alloys can absorb a great deal of energy before mechanical failure. Infrequently, parts in service made of Ni-Cr-Mo alloys would become brittle or develop cracks below the nominal UTS. Two of these EAC inducing environments are hot caustic and hot wet hydrofluoric acid. [1-2] These environments also cause EAC in austenitic stainless steels, and relatively nickel alloys are more resistant than austenitic stainless steels in these two environments.

Hot Concentrated Chloride Solutions (Oil and Gas Applications)

One of the major limitations of stainless steels is that these alloys are susceptible to chloride induced localized attack such as crevice corrosion, pitting corrosion and stress corrosion cracking. Ni-Cr-Mo alloys are the most resistant Ni based alloys to the classic chloride induced localized corrosion that troubles the stainless steels. In some cases SCC was reported in high strength materials; however, cracking only occurred in very aggressive conditions, such at temperatures higher than 200°C, pH lower than 4 and presence of hydrogen sulfide. [14] U-bend specimens of C-2000, C-22 and C-276 alloys were not susceptible to cracking in boiling (154°C) 45% $MgCl_2$ solution after 1008 h of testing. [15] It was also reported that C-276 and C-4 alloy were free from cracking in a 25% NaCl solution at 232°C; however, these alloys were susceptible to cracking in a $MgCl_2$ solution of same chloride content at the same temperature. [16] Alloy 22 alloy was immune to SCC in 20.4% $MgCl_2$ solution up to 232°C, even in the 50% cold reduced condition and in the 50% cold reduced plus aged at 500°C for 100 h condition. [15]

Extensive EAC research has been conducted using Ni-Cr-Mo and other corrosion resistant alloys regarding their application in gas and wells, mainly as OCTG (oil country tubular goods). An excellent review of the corrosion problems associated with oil and gas production has been published. [17] This review covers all types of corrosion (including EAC) and all type of materials including Ni-Cr-Mo alloys such as C-276 and 625. [17] The most common environmental cracking in oil and gas applications are sulfide stress cracking and hydrogen embrittlement. Many wells involve increasingly aggressive conditions, namely temperatures as high as 230°C, high chloride concentrations (151,705 ppm or ~15% Cl⁻) and low pH due to the presence of hydrogen sulfide in the system and the injection of carbon dioxide for recovery purposes. [18] Most mill annealed Ni-Cr-Mo alloys have a hardness of HRB 90 (Rockwell Hardness B) and therefore are not strong enough to be used in deep wells. Therefore, tubular and other components are usually fabricated using cold worked materials for increased strength. It is known that harder materials (with higher yield strengths) are generally mores susceptible to EAC than mill annealed materials. Therefore, NACE International Materials Requirement MR0175 lists the maximum hardness allowed per each alloy to avoid the possibility of stress cracking in the field. [19] For example, for alloys C-276 and 625, the maximum allowed hardness is HRC 35, but for alloy 686 the maximum allowed hardness is HRC 40. [18-19] Alloy C-276 is more resistant to cracking than alloy 625. [17-18] Ranges of tolerance for alloys C-276, 625 and others regarding temperature, pH, chloride concentration, partial pressure of hydrogen sulfide and carbon dioxide have been published in great detail. [18] It has been reported that the resistance to stress corrosion cracking of Ni-Cr-Mo alloys increase as their pitting resistance equivalent number (PREN) increase. [17-18] This correlation exists and it has been attributed to cracks nucleating at corrosion pits, which not only provide an even more aggressive environment but also act as stress concentrators. [18] In many cases, (such as in components with thick sections), the strength of the Ni-Cr-Mo alloys cannot be increased by using cold working. In these instances, alloys such as 725HS and 22HS (HS for high strength) can be used. These alloys are heat treatable, producing a finely dispersed second phase, which approximately doubles their yield strength. [13,20]

Ni-Cr-Mo alloys are also resistant to EAC in seawater applications including stress corrosion cracking, hydrogen embrittlement and corrosion fatigue. For example, cold-worked alloy 686 maintained its ductility under cathodic polarization in synthetic seawater both under slow strain rate testing and constant load of notched specimens. [21] Similarly cold-worked alloy 686 had practically the same fatigue crack growth (or endurance) in sea water than in air. [21]. This again proves that Ni-Cr-Mo alloys are extremely resistant to EAC in chloride environments even under the most severe testing conditions.

Hot Caustic Solutions

Nickel-based alloys as well as austenitic stainless steels are known to be susceptible to caustic cracking. Most of the research of caustic cracking of nickel alloys was dedicated to the family of Ni-Cr-Fe alloys such as alloys 600, 690 and 800 due to their importance in the nuclear power generation industry. [22] The amount of published data regarding the EAC behavior of Ni-Cr-Mo alloys is more limited. Under slow strain rate testing (SSRT) conditions, C-276 alloy was susceptible to transgranular cracking in 50% NaOH at 147°C. [23] Thermal treatment of alloy C-276 (aging for 1 h at 871°C) did not change the cracking mode or susceptibility under the same testing conditions. [23] When alloy C-276 was tested in the same solution using the C-ring method of applying load, cracking was absent and only serrations in the specimens were observed. [23] On the other hand, 50% cold reduced alloy C-276 was not susceptible to cracking under SSRT conditions but was susceptible under C-ring testing conditions. The susceptibility to cracking of Ni-Cr-Mo alloys in hot caustic solutions may be dependent not only on the type of alloy but also on the mode of applying the tensile stresses. For example, mill annealed and also thermally aged for 24 h at 677°C C-shape specimens (ASTM G 39) of C-22 alloy did not exhibit cracking after immersion in 50% NaOH solution at 147°C for 720 h. [24] Ni-Cr-Mo alloys are heavily alloyed since they

contain approximately 40% in weight of these alloying elements (Table 1). For caustic applications, it is not recommended the use of alloyed nickel since commercially pure nickel (such as Ni-200 or N02200) perform better than Ni-Cr-Mo alloys regarding corrosion resistance. [5] Therefore, it is unlikely to find caustic cracking of Ni-Cr-Mo alloys in service, except in rare conditions such as plate heat exchangers that may need a material resistant to caustic corrosion on one side and resistance to localized corrosion by chlorides on the other side.

Hot Wet Hydrofluoric Acid Solutions

Nickel alloys as well as austenitic stainless steels are susceptible to EAC in wet hot HF solutions. [7] Nickel alloys are less susceptible than stainless steels to cracking and all nickel alloys are not equally susceptible. For example, alloy 400 (Ni-Cu) is extremely resistant to cracking under reducing conditions but suffer intergranular attack and stress corrosion cracking under oxidizing conditions. [7]

Pawel tested several nickel engineering alloys for resistance to cracking in HF environments using U-bend specimens. [25] Tests using C-276 U-bends were carried out in 1% HF and 10% HF at 24°C and 50°C and in 10% HF at 76°C for 48h. It was reported that none of the tested C-276 specimens suffered EAC. In another series of tests, U-bend type of specimens of Alloys C-276, 22 and 686 were exposed for up to 100 h to a HF gas stream both at 50°C and at 70°C. [26] The HF concentration is not known. None of these three alloys suffered EAC under the testing conditions. The general corrosion rate at 50°C was higher than at 70°C, probably because more condensation occurred. [26]

Laboratory testing using U-bend specimens (ASTM G 30) showed that Ni-Cr-Mo alloys such as C-276, C-22 and C-2000 alloy were susceptible to SCC in hot wet HF. [7,15] After testing for 10 days (240 h) in 20% HF, alloy C-276 did not suffer cracking at 66°C, neither in the vapor or liquid phases but suffered rather generalized cracking at 93°C. At 93°C, cracking was twice as deep in the liquid phase than in the vapor phase. However the transgranular type of cracking remained the same (Figures 1 and 2). Under the same testing conditions, alloy 2000 was resistant to cracking at 66°C both in the liquid and vapor and at 93°C it was resistant to cracking in the vapor phase. [7] Alloy 2000 suffered cracking in the liquid phase of 20% HF at 93°C (Figure 3). The cracking appearance of Alloy 2000 was different than that of Alloy C-276, the cracks were thinner and the metal seemed to have developed internal voids in the cracked area (Figure 3). In a similar set of tests, Alloys 625, 22 and 2000 were exposed to 20% HF at 93°C for 336 h. Alloy 625 did not develop cracks probably due to the high general dissolution rate of this alloy of near 50 mm/year. Alloy 22 developed cracks both in the liquid and vapor phases and again, the cracks were twice as long in the liquid phase than in the vapor phase. The mode of cracking of Alloy 22 was similar to that of Alloy C-276 (Figures 1 and 2). Compared to the high rates of alloy 625, the general corrosion rate of Alloy 22 was less than 2 mm/year. Similar to Alloy 22, Alloy 2000 developed cracks also in the liquid and vapor phases of 20% HF at 93°C and again the cracks were twice as long in the specimen exposed to the liquid phase. [7] The general corrosion rate of Alloy 2000 was less than 500 µm/year. The cracking mode of Alloy 2000, although still transgranular, was different from Alloys 22 and C-276 since the former had less branching and the metal exhibited internal voids in the cracked area. The data just described show the beneficial effect of Cr in the resistance of Ni-Cr-Mo alloys, especially in the vapor phase. [7] Also, it is undeniable that a small amount of Cu in Alloy 2000 changed the mode of cracking and reduced the susceptibility to EAC. [7]

U-bend specimens of Alloy 59 (N06059) were tested for resistance to EAC in aerated and deaerated 20% HF at 25°C and 50°C. [27] It was reported that none of the U-bend specimens showed any indication of EAC after an exposure time of 200 h. [27] In the same study, Alloy 50 was tested by the SSRT technique using a deformation rate of 9.8×10^{-7} s^{-1} in 20% HF at 25°C. The potential was controlled at four different values, 0, 50, 100 and 150 mV$_H$. Only the Alloy 59 specimen strained at the lowest potential (0 mV$_H$) suffered EAC since it had a reduction in area of 45% when the reduction in area in air was 67%.

[27] The authors attributed this EAC failure to hydrogen uptake by the alloy. The corrosion potential (E_{corr}) of Alloy 59 in deaerated 20% HF at 25°C was reported to be approximately +50 mV$_H$. [27] When the HF solution was aerated, Ecorr was approximately +175 mV$_H$.

Super Critical Water Oxidation (SCWO)

Since Ni-Cr-Mo alloys such as C-276 and 625 have a high corrosion resistance, its applicability in supercritical water oxidation (SCWO) processes was investigated. SCWO is used to treat waste (especially aqueous solutions containing small amount of organic compounds). The supercritical conditions of pure water are 374°C and 221 atm. It has been reported that components made of Alloy C-276 suffered intergranular stress corrosion cracking in laboratory trials aimed to the destruction of methylene chloride. [28-29] It has been reported that when the waste contained chloride (such as in methylene chloride) the degradation of the Ni-Cr-Mo alloy was more pronounced that when the organic waste did not contain chloride (such as in methanol). [28-29] It was also reported that the system seemed more aggressive just below the critical point, when the water was still in liquid state. [28-30]

Tests were conducted using Alloy 625 tubes, pressurized up to 38 MPa, heated at one end to 500°C and kept the other end at ambient temperature. [31] An oxygenated sulfuric acid solution (up to 0.2 M) was circulated through the tube for times as long as 155 h. Alloy 625 suffered intergranular cracking at temperatures above 200°C. When temperatures exceeded 300-350°C, the intergranular attack was less severe and appeared mainly in the vapor phase of the system. At even higher temperatures (>430°C), the attack was more generalized without intergranular cracking. [31] Alloy 625 suffered even more severe intergranular cracking, especially originating from the bottom of pits, when up to 0.1 M oxygenated hydrochloric acid was used instead of sulfuric acid. [31-34] In some cases the Alloy 625 tubes perforated in a day by intergranular stress corrosion cracking in the temperature region of 280°C. [32] Even in the hydrochloric acid feed, the corrosion of Alloy 625 was not as severe when the temperature was higher than 380°C. [32] Similar results regarding temperature ranges of aggressiveness were reported for Alloy 625 when the feed was loaded with nitric acid. [34] However, nitric acid did not seem to produce deep intergranular cracks. [34] These tests [31-34] again confirm that the presence of chloride ions makes the solution more aggressive and that the most deleterious conditions for Ni-Cr-Mo alloys in SCWO processes are in the sub-critical conditions (such as pre-heater and coolers), not at the actual reactor operating conditions.

A SCWO tube reactor was fabricated using alloy C-276 and put into service for only 24 h when it failed (through wall perforation) due to intergranular stress corrosion cracking. [35] The feed to the tube was deionized water mixed one to one with organic oil. The mixture did not have chlorides but did have bromine. [35] Cracking occurred only in the zone of the tube subjected to sub-critical temperatures. Since chloride was not present the authors hypothesized that the tube failed by a caustic-like mechanism. [35]

Slow strain rate testing (SSRT) was carried out using Alloy 625 (and five other austenitic alloys) in deaerated supercritical water at 500°C and 25.5 MPa pressure. [36] The dissolved oxygen content was less than 10 ppb and the conductivity of the water was kept at less than 0.1 μS/cm. Extensive intergranular stress corrosion cracking was reported for Alloy 625. [36] In general, laboratory tests seem to suggest that Alloy 625 will suffer intergranular stress corrosion cracking both in sub-critical and super-critical water conditions.

Environmentally Assisted Cracking of Alloy 22

Because of its excellent resistance to stress corrosion cracking and other types of localized corrosion, Alloy 22 (N06022) was selected by the Department of Energy (U.S.A.) to fabricate the outer shell of the high level nuclear waste containers to be disposed permanently at the Yucca Mountain site. [37-39] Alloy

22 has been extensively tested for its susceptibility to SCC in a variety of environments, mainly at GE Global Research, Southwest Research Institute and Lawrence Livermore National Laboratory (LLNL). This alloy was found extremely resistant to EAC in many different solutions at the corrosion potential, at all the tested temperatures from ambient to 110°C. [40-43] Tests were carried out using cyclic loading, constant load, constant deformation and slow strain rate tests in solutions from 14 molal $MgCl_2$, to simulated concentrated ground waters from pH 3 to 13. U-bend specimens of Alloy 22 (N06022) and other Ni-Cr-Mo alloys such as C-4 (N06455) and 625 (N06625) were used to characterize their stress corrosion cracking susceptibility in a variety of environments. [44] Gas Tungsten Arc Welded (GTAW) and non-welded U-bend specimens were exposed for more than 5 years at the corrosion potential to the vapor and liquid phases of three different solutions (pH 2.8 to 10) simulating up to 1000 times the concentration of ground water both at 60°C and 90°C. None of these Ni-Cr-Mo alloys suffered any indication of environmentally induced cracking. [44] Alloy 22 was found susceptible to EAC when SSRT was performed on mill-annealed specimens in hot simulated concentrated water (SCW) at anodic applied potentials. [43,45,46] SCW is a multi-ionic alkaline solution approximately 1000 times more concentrated than a Yucca Mountain ground water. It is likely that the small amount of fluoride ions present in this solution (1400 ppm) contributed to the cracking of C-22. [46] The susceptibility to cracking of Alloy 22 was strongly dependent on the applied potential and the temperature of the solution. The highest susceptibility to EAC was found at around 90°C at +400 mV in the saturated silver chloride (SSC) electrode scale. [46] At the corrosion potential, Alloy 22 was free from EAC even at 90°C. Similarly, at anodic applied potentials, Alloy 22 was free from EAC at ambient temperatures and as the temperature increased the time to failure in the tests decreased. [46] It has also been reported that Alloy 22 (N06022) may suffer some embrittlement when it is slowly strained under cathodic applied potentials (or currents). [46-48] The maximum susceptibility to cracking under cathodic conditions seemed to occur at ambient temperatures suggesting a hydrogen related failure mechanism for this Ni-Cr-Mo alloy.

Hydrogen Embrittlement

It has been mentioned above that Alloy 22 may be susceptible to hydrogen embrittlement when strained at cathodic potentials in an aqueous solution at ambient temperatures. [46-48] Other Ni-Cr-Mo alloys such as Alloy 625 and C-276 may also suffer hydrogen embrittlement, especially in the thermally aged condition when these alloys lose their solution-annealed ductility (Table 1). It has been claimed that Alloy 625 suffers hydrogen embrittlement at ambient and high temperatures. [49-50] It has also been indirectly assessed that Alloy C-276 would be more prone to hydrogen embrittlement than Alloy 625 because the former offers more irreversible trapping sites for hydrogen. [51] A series of tests were conducted using U-bend type specimens made of Alloy C-276 (and other alloys), which were charge with hydrogen in a 5% sulfuric acid solution. Tests were carried out using as-received material and also 50% cold worked and cold worked plus aging at 500°C. Alloy C-276 was found more prone to hydrogen embrittlement than for example 316L stainless steel. [52] Additionally, it was reported that Alloy C-276 increased it susceptibility to hydrogen embrittlement when it was cold worked and thermal aged. [52] The same observation on the effect of cold working and thermal aging was also made by Rhodes. [17]

Effect of Second Phase Precipitation

When Ni-Cr-Mo alloys are aged at temperatures higher than approximately 600°C for long time, long range ordering reactions and precipitation of tetrahedrally close packed (TCP) phases (μ, P, σ) may take place. The presence of the TCP phases produced by thermal aging may greatly reduce the ductility of Ni-Cr-Mo alloys. For example, for annealed C-276 alloy, the yield stress (YS) at room temperature is 360 MPa, the ultimate tensile stress (UTS) is 807 MPa, the elongation to rupture is 63%; however, for a

C-276 alloy that was aged for 16,000 h at 760°C, the YS increased to 476 MPa, the UTS increased to 894 MPa and the elongation to rupture decreased to 10%. [5] At the same time, the impact energy (Charpy) is reduced to a few ft.lb. Thermally aged Ni-Cr-Mo alloys are even more susceptible to EAC since they become brittle (lose ductility) even in air. Indeed, it has been reported that thermally aged Alloy C-276 was more susceptible to hydrogen induced cracking in environments containing hydrogen sulfide (H_2S) than non-aged material. [53-54]

SUMMARY

1. Most of the EAC data for Ni-Cr-Mo alloys are for Alloys C-276 and 625
2. Ni-Cr-Mo Alloys are highly resistant to EAC in concentrated hot chloride solutions
3. Ni-Cr-Mo Alloys suffer EAC in hot wet HF solutions, in hot concentrated caustic solutions and in super critical water applications
4. Ni-Cr-Mo Alloys are susceptible to hydrogen embrittlement, especially if thermally aged
5. The same environments which produce cracking in Ni-Cr-Mo alloys also produce cracking in austenitic stainless steels

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TABLE 1
APPROXIMATE CHEMICAL COMPOSITION AND TYPICAL MECHANICAL PROPERTIES
OF CORROSION RESISTANT Ni-Cr-Mo ALLOYS

Alloy	UNS	Approximate Composition	YS 0.2% (MPa)	UTS (MPa)	ETF (%)
C-276	N10276	59Ni-16Cr-16Mo-4W-5Fe	347	741	67
C-4	N06455	65Ni-16Cr-16Mo	335	805	63
Alloy 625	N06625	62Ni-21Cr-9Mo-3.7Nb	535	930	45
Alloy 22	N06022	59Ni-22Cr-13Mo-3W-3Fe	365	772	62
Alloy 2000	N06200	59Ni-23Cr-16Mo-1.6Cu	345	758	68
Alloy 59	N06059	59Ni-23Cr-16Mo-1Fe	340	690	40
Alloy 686	N06686	46Ni-21Cr-16Mo-4W-5Fe	364	722	71
Alloy 21	N06210	60Ni-19Cr-19Mo-1.8Ta	370	775	64
Alloy 22HS *	NA	61Ni-21Cr-17Mo	742	1232	50
Alloy 725HS *	N07725	57Ni-21Cr-8Mo-9Fe- 3.4Nb-1.4Ti	1043	1375	25

Mechanical Properties at ambient temperature YS = Yield Strength, UTS = Ultimate Tensile
Strength, ETF = Elongation to Failure, NA = Not Available, * Age Hardened

FIGURE 1 - SCC of Alloy C-276 (N10276) U-bend specimen immersed in a
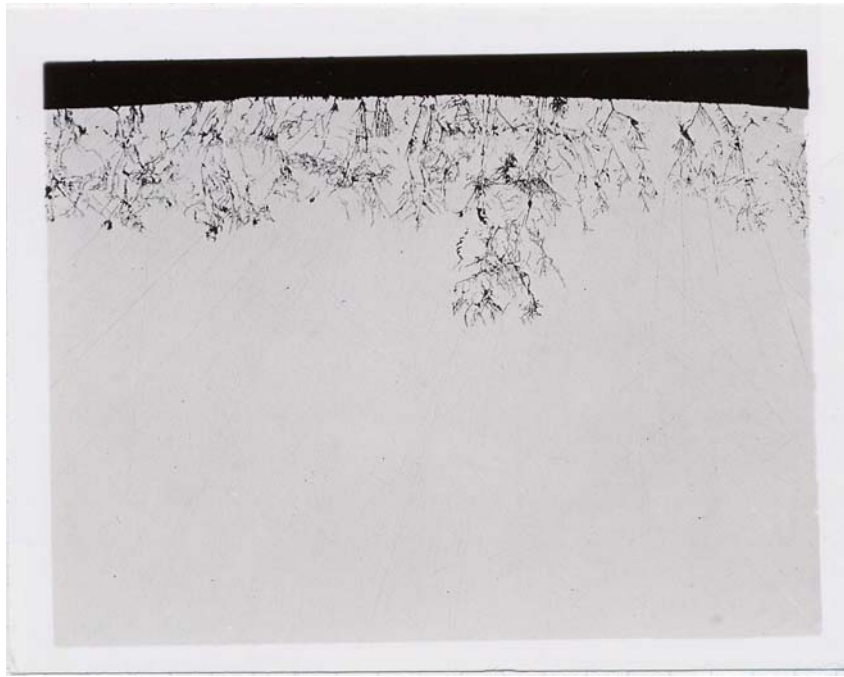Liquid 20% HF solution at 93°C for 240 h. Magnification X100

FIGURE 2 - SCC of Alloy C-276 (N10276) U-bend specimen immersed in the vapor area of a
20% HF liquid solution at 93°C for 240 h. Magnification X100

FIGURE 3 - SCC of Alloy C-2000 (N10276) U-bend specimen immersed in a
Liquid 20% HF solution at 93°C for 240 h. Magnification X100